

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



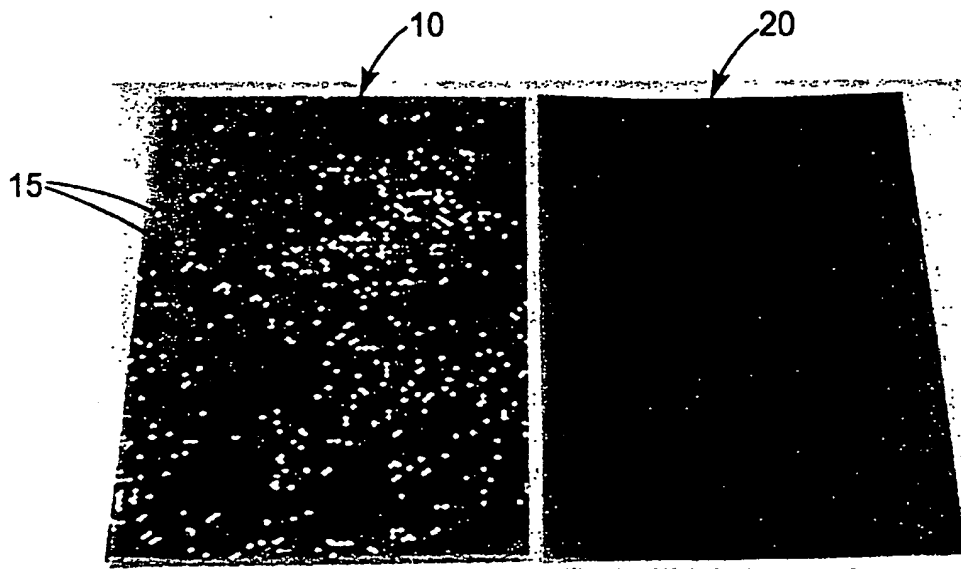
(43) International Publication Date
1 November 2001 (01.11.2001)

PCT

(10) International Publication Number
WO 01/81491 A1

- (51) International Patent Classification⁷: C09J 7/02, 201/00
- (21) International Application Number: PCT/US00/24444
- (22) International Filing Date:
6 September 2000 (06.09.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
09/558,663 26 April 2000 (26.04.2000) US
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- (81) Designated States (*national*): AE, AG, AL, AM, AT, AT (utility model), AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, CZ (utility model), DE, DE (utility model), DK, DK (utility model), DM, DZ, EE, EE (utility model), ES, FI, FI (utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KR (utility model), KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (utility model), SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: LATEX ADHESIVE WITH COATING ENHANCER



(57) Abstract: A coatable adhesive comprising a latex adhesive and a coating-enhancing amount of a linear or branched, optionally unsaturated mono-alcohol. Methods of improving the coatability of latex adhesives, and composites comprising adhesives that have been coated with such latex adhesives are also provided. Structured liner composites particularly benefit from such alcohol additives, which further may be optionally be interrupted with one or more oxygens.



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LATEX ADHESIVE WITH COATING ENHANCER

Field of the Invention

5 This invention relates to coatable adhesives. More specifically, this invention relates to coatable latex adhesives.

Background

10 Applying water-based coatings or adhesives on low energy surfaces has always been a difficult challenge. The crux of the problem is that water is a high energy liquid and does not readily wet-out a low energy surface. This results in water-based coatings beading up into droplets on the low energy surface, similarly to how water "beads up" on the hood of a new car.

15 A number of methods are known in the art to alleviate this situation. One method is to raise the surface energy of the substrate by using chemical prime layers, or using energetic methods such as Corona Treatment or Flame Treating. A second method is to lower the dyne level of the water-based coating, by adding natural soaps or synthetic surfactants. Many types are known in the art. A third method is to raise the viscosity of the solution so that the liquid has sufficient modulus to maintain a continuous film by physically resisting the forces that would
20 cause it to break into droplets. This third method is typically useful only when used in conjunction with one of the first two methods. A related method is to coat a thicker layer of adhesive, which can have a similar effect as raising the viscosity. However, this is generally an unacceptable method from both a cost and performance point of view. Adding common organic solvents such as methyl ethyl
25 ketone ("MEK") or toluene is also an option to improving coatability, but this method has some deleterious effects on the water-based adhesive, some of which include making the solution flammable, negatively impacting the "eco-friendly" aspect of the water-based adhesive, and destabilizing the latex particles, thus causing coagulation.

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Summary of the Invention

The present invention provides a coatable adhesive comprising a latex adhesive and a coating-enhancing amount of a linear or branched, optionally unsaturated mono-alcohol. The alcohol is a liquid at 25°C. Also provided are methods of improving the coatability of latex adhesives, and composites comprising adhesives that have been coated with such latex adhesives. An additional embodiment of the present invention provides an adhesive/structured liner composite, wherein the alcohol may additionally optionally be interrupted with one or more oxygens.

Brief Description of Drawing

Fig. 1 is a side-by-side photograph of adhesives coated on a non-flat liner.

Detailed Description

The invention in this document pertains to the use of linear alcohols as a coating additive to water-based adhesives to get defect-free web when coating on low energy surfaces such as silicone-coated release liner. Small amounts of a linear alcohol such n-Octanol can have a dramatic effect on the coating performance of a water-based adhesive. This is particularly true, when microstructured liners, such as ComplyTM liner are used. Surprisingly, the use of the coating-enhancing alcohol additive has little or no adverse effect on adhesion performance as compared to the same adhesive formulations that do not contain the coating-enhancing alcohol additive. Preferably, the 180° peel value of the inventive adhesive is no less than 80% of the same adhesive formulations that do not contain the coating-enhancing alcohol additive. The present invention additionally can enable an adhesive that can be satisfactorily coated at low speeds with few or no defects to be modified so that it can be coated at high speeds, with few or no defects while not sacrificing adhesion performance.

Coating a low energy surface, such as a release liner, with a latex adhesive is difficult. If modifications to the adhesive or the low energy surface are not taken, the adhesive will not remain evenly coated over the low energy surface.

Rather, the adhesive will tend to "bead up" on the surface, causing unevenness and discontinuities of the adhesive on the surface.

A typical release liner construction consists of a paper, film or paper/film composite with a surface layer that typically contains silicone or fluorochemical moieties. The objective of this layer is to provide a surface that will allow an adhesive to be easily removed with minimal force. Many examples abound of this type of construction, such as pressure-sensitive adhesive ("PSA") backed labels or decals.

Since the function of a release liner is to provide a surface that will weakly bond to the adhesive, modifying this layer to increase its surface energy is generally not an option. Surface treatments will modify the bonding properties and thus negate the purpose of using a release surface in the first place. The result is that all of the modifications must come from the water-based adhesive.

Of the methods described earlier, viscosity modification is perhaps the easiest to implement with minimal deleterious effects to the final adhesive or coating properties. However, most common coating technologies have an optimum range of rheological characteristics for efficient coating performance. While these viscosity ranges vary from one coating technology to another, the optimum viscosity for coating is generally lower than what is needed to prevent the coating from dewetting on a release liner. Further, even if the coating technique can be adjusted to handle a higher viscosity, coating performance usually suffers. In addition, a high viscosity coating will generally have more defects due to entrained air and ribbing (high & low areas). Dried particles of the adhesive also become more prevalent due to poor circulation of the liquid adhesive in the coating equipment.

The above comments on viscosity also cover the art of modern rheology management where the viscosity can be adjusted to vary the viscosity versus shear rate. Much is known in the art, and many products are available to adjust the rheology of the water-based adhesive or coating. The most common additives allow for dramatically decreasing viscosity versus increasing shear rate. Despite these additives, the problems discussed above still remain. One key aspect is called the recovery time for the adhesive to build back to its low shear viscosity

after being exposed to high shear such as when being pumped. A short recovery time is needed in order to have the high viscosity needed to prevent dewetting of the adhesive on the release liner. However, a longer recovery time is needed to permit the adhesive coating to level and for air bubbles to be released.

5 The method of adding surface active agents (surfactants) to the water-based adhesive is also known in the art. This method works by lowering the energy level (dyne level) of the adhesive to more closely match the low energy surface. While many materials are available to carry out this method, they suffer from a number of disadvantages. The first is that all surface-active agents cause foaming. While the
10 degree of foaming varies from one product to another, foam generation is a problem due to the fact that it results in poor appearance and performance of the final product, and the foam also interferes with the efficient coating of the adhesive. In addition, addition of surfactants generally results in more moisture sensitivity of the adhesive. While this may not be a problem for PSA backed
15 nametags, this is a problem for decals and related products that are used in an outdoor environment such as graphics on the side of a truck, where the lower adhesion due to moisture sensitivity is a major product defect. Another problem is that surface-active agents also preferentially migrate to the surface of the adhesive. This will change the bonding characteristics of the adhesive, particularly for PSAs.
20 The most likely points of failure are between the backing and the adhesive, or the adhesive and the substrate. When combined with the moisture sensitivity problem described above, one can see that a catastrophic failure can result.

 One can argue that to counteract the foaming problem, antifoam agents can be added. While judicious use of antifoaming agents can improve a coating
25 situation, they also suffer from a number of problems. One is that many antifoam agents only work temporarily, and thus are best added just before coating. Giving control of these additives to a coater operator will result in the problem of too much being used. Since many of these antifoaming agents are surface active, care must be taken when adding them to a water-based formulation. Long-lasting
30 antifoaming agents are available, but most of these are based on silicone technology. Silicones have severe detrimental performance on adhesives, and are generally not used in PSAs. Further, all antifoam agents are surface active,

meaning they will affect adhesive bonding performance. Thus, the combination of surfactants and antifoaming agents has many negative effects, and both are generally used in the smallest possible amounts.

5 The method of using common solvents such as MEK are generally not used simply because most water-based adhesives will be destabilized by such solvents. Further, improving the bond between the adhesive and a release liner is not desirable.

10 The situation of coating a release liner is further complicated when the release liner surface is no longer flat, but has a three-dimensional shape, such as the liner used in the Comply™ products sold by Commercial Graphics. Such a release liner presents a number of unique problems: first is the fact that the three-dimensional surface results in an adhesive coating layer that has thick and thin spots. The thin spots are of particular concern because there is more likelihood of the adhesive starting to dewet at the thin spots. Thus, the coating must be
15 engineered to prevent dewetting at the thinnest areas. A second fact is that the adhesive rheology must be adjusted to allow coverage of the entire topography. For example, in the Comply™ liner case, the liner surface consists of square pockets separated by a series of intersecting ridges, similar in geometry to graph paper, where the lines represent the ridges. These pockets must be completely filled with
20 adhesive in order to have optimum adhesive performance. A very high viscosity adhesive would have problems in filling these depressed squares. A third fact is that certain areas of a three-dimensional topography are more likely to trap air bubbles during the coating operation. For the Comply™ liner example, this is most likely to happen at the intersections of the ridges. The trapped air bubbles present
25 two difficulties. One is that they result in aesthetic and performance problems. Second is that an air bubble near a ridge is likely to cause a defect that results in dewetting on the low energy surface.

When confronted with a 3-dimensional liner topography, one can quickly see how the existing solutions to coating a low energy surface are found wanting.
30 Increasing the viscosity results in incomplete fill of the topography, which in turn affects adhesive performance and the performance of the topography that was designed into the product. Further, more air will be trapped, creating more bubbles

that will lead to defects. Thus, one can see that rheology alone is not the answer. Surfactants have all the problems described earlier, plus on a three-dimensional surface they will stabilize bubbles that are formed. This occurs not only in the coated layer of adhesive, but also causes a buildup of bubbles in the adhesive reservoir (coating pan) that most coating technologies use. Common organic solvents have all the problems listed earlier.

“Coating-enhancing” means that the adhesive exhibits improved coating uniformity without detracting from the adhesive bonding performance properties as compared to the same adhesive composition without the alcohol.

As used herein, “latex” means an emulsion of rubber or plastic globules in water. Preferred latex adhesives are styrene-butadiene rubber, acrylic, neoprene and vinyl acetate-ethylene. Additional preferred latices include butadiene and acrylonitrile copolymers, butadiene with styrene and acrylonitrile, chloroprene copolymers, methacrylate and acrylate ester copolymers, vinyl acetate copolymers, vinyl and vinylidene chloride copolymers, ethylene copolymers, fluorinated copolymers, acrylamide copolymers, styrene-acrolein copolymers, pyrrole and pyrrole copolymers, and poly(vinyl acetate)-poly(vinyl alcohol) copolymers.

The latex adhesive may also contain appropriate adjuvants such as plasticizers, tackifiers, viscosity modifiers, solvents (e.g. to coalesce the emulsion particles), fillers, humectants, biocides and anti-foaming agents.

As used herein, the term “low energy surfaces” is intended to mean those surfaces which exhibit low polarity and low critical surface tension (less than about 40 dynes/cm²) characteristics. Examples of low energy surfaces include polyolefin plastics, glass, and liners made of kraft papers, polyethylene, polypropylene, polyester or composites of any of these materials. These liners are coated with release agents such as fluorochemicals or silicone. U.S. Patent No. 4,472,480 describes low surface energy perfluorochemical liners. The preferred liners are papers, polyolefin films, or polyester films coated with silicone release materials. Examples of silicone coated release papers are PolyslikTM silicone release papers supplied by Rexam Release Corp., and silicone coated papers supplied by Daubert Chemical Co. (Dixon, IL). Particularly preferred low energy surfaces are structured liners, i.e. non-flat liners that impart roughness, grooves or other texture

to the adhesive that is cast on the low energy surface. Most preferred are the structured liners that impart channels or other geometries to the adhesive that allow escape of air upon placement of the adhesive on a smooth surface after removal of the protective low energy surface material. Particularly preferred structured liner configurations are disclosed in US Patent No. 5,897,930.

The adhesive composite embodiment of the present invention also contains a backing, which is the item to be adhered to the ultimate substrate by the latex adhesive. Suitable backings include, but are not limited to, polyesters, polyolefins, papers, cardboard, foils, polyacrylates, polyurethanes, perfluoropolymers, polycarbonates, ethylene vinyl acetates, and the like including multilayer films and combinations. Backings of vinyl films, woven and nonwoven sheets, woven and nonwoven fabrics, papers and retroreflective sheeting are particularly preferred.

The following non-limiting examples are provide for illustrative purposes only, and are not intended to limit the scope of the present invention. Unless otherwise indicated, all ratios and percentages are by weight, and all molecular weights are weight average molecular weights.

Peel Test: Adhesion tests were a modification of ASTM method D3330 (1992) and Pressure Sensitive Tape Council method PSTC-1 (1989). Painted aluminum test panels (Fruehauf, Indianapolis, IN) were cleaned with DuPont "PrepSol" and allowed to dry. Samples of pressure sensitive adhesive and film on liner were cut into 2.54 centimeter wide strips. The release liner was removed, and the strips were applied to the panels using either a PA-1 Hand Applicator (available from Minnesota Mining and Manufacturing Company (3M) St. Paul, MN) at a speed of about 2.5 centimeter/second or a Vanquisher roll laminator (Stoughton Machine and Manufacturing Co., Inc., Stoughton Wisconsin) at 40 psi gauge pressure and a speed of about 2.5 cm/second. A backing strip of 2.54 centimeter wide 3M Scotchcal™ Film Series 3650 adhesive film was laminated in registration onto each sample strip. The backing film prevented the sample films and pressure sensitive adhesive from excessively stretching during peel back testing. After 7 days of soaking the applied samples in water at 22°C, the samples were removed from the water and the peel adhesion was measured as a 180 degree peel back at a

crosshead speed of 30.5 centimeters per minute using a Lloyd 500 tensile tester (Lloyd Instruments, Segensworth Fareham England). The reported peel adhesion value is an average of three peel adhesion measurements.

5 Standard Defect Evaluation. To determine the ability of an adhesive to coat on a non-flat liner, a latex adhesive is coated on a 90 lb. polyethylene-coated paper liner from Assi-Domaem/Inncoat GmBh, (Craubling, Germany) to which has been imparted a structured surface as described in Example 3 of US Patent No. 5,897,930 at a consistent wet coating thickness of about 75 micrometers. The dry
10 coating thickness depends on the % solids of the adhesive. In general, most adhesives were coated at 40% solids, which in turn gives a dry coating weight of 0.38 +/- 0.02 grams per 154.8 cm² (a 4" x 6" sample). Preferably, the adhesive exhibits less than 50 defects per 154.8 cm² (a 4" x 6" sample). Preferably, the alcohol is present in an amount such that said adhesive exhibits fewer defects as
15 compared to the same adhesive formulation that does not contain the coating enhancing alcohol.

Examples

20 Example 1. 3M FASTBOND™ 49 adhesive was mixed with 0.1% of CE-2N Black pigment (Ciba-Geigy, Hawthorne, NY) to provide a gray color in order to see defects. To this mixture, 2.5% by weight of n-Octanol (Eastman Chemical Co., Kingsport, TN) was added while stirring on an air powered mixer with a 3-blade propeller style mixing blade. The mixing speed was set to give a slight vortex without causing air entrainment. The n-Octanol was added slowly so as not
25 to "shock" the adhesive and cause coagulation. The viscosity was measured with a Brookfield LVT viscometer with a #2 spindle at 30 RPM. The viscosity was recorded as 450 cps. The liquid was then coated on Comply™ liner SCW1007 (3M Co., St. Paul, MN) using a knife bar coater with a coating gap of nominally 75 micrometers. The sample was dried for 10 minutes at 65°C. The dried coating
30 weight was measured on analytical balance was found to be 0.50 grams per 154.8 cm². The liner coated was then laminated to a multilayer clear olefin film. A

representative 4" by 6" sample was then cut out the construction, and the number of defects were counted. The number for this sample was zero defects.

5 Comparative Example 1. Same as example 1 except that no n-Octanol was added to the formulation. The measured viscosity was 430 cps. The number of defects was 495.

10 Example 2. 72 grams of 3M FASTBOND™ 49 adhesive was mixed with 27 grams of DI water, 0.15 grams of CE-2 black, 1 gram of 28% ammonia water, 0.5 gram of Acrysol ASE-60 (Rohm & Haas Co., Philadelphia, PA), and 2.5 grams of n-Octanol. Procedures were the same as in Example 1. The viscosity was 200 cps. Coating in the same fashion as in Example 1, the dried coating weight was 0.37 grams per 154.8 cm². There were two defects. The objective of this example was to coat at the same wet coating thickness, but have a lower dried coating weight of
15 adhesive.

Examples 3 to 5. Same as Example 2, but the amount of ASE-60 was increased to 1.0, 1.5 and 2.0 grams respectively. All samples had 0 defects. See Table 1.

20 Comparative Example 2 to 5. Same as Examples 2 to 5, except no n-Octanol. See Table 1 for results.

TABLE 1

Example #	n-Octanol (%)	ASE-60 (gm)	Viscosity (cps)	Ctg. Wt. (gm)	Defects
2	2.5	0.5	200	0.37	2
3	2.5	1.0	295	0.37	0
4	2.5	1.5	490	0.37	0
5	2.5	2.0	780	0.37	0
Comp Ex 2	0	0.5	165	0.37	Approx. 3000
Comp Ex 3	0	1.0	235	0.37	Approx. 5000
Comp Ex 4	0	1.5	400	0.37	435
Comp Ex 5	0	2.0	660	0.36	196

As may be seen from table 1, n-Octanol provides enhanced coatability over a range of viscosity levels to few or no defects. In contrast, the control samples with no n-Octanol have large numbers of defects, even with increased viscosity. As will be shown the next 4 examples, higher viscosity alone does not guarantee coating quality.

Examples 6 and 7. In these examples, a Changeable Graphics Adhesive, comprising a blend of FASTBOND™ 49 and microspheres, was modified with 2.5% n-Octanol to improve coating of this adhesive on Comply™ liner in a production process. The only other change was to lower the amount of ASE-60 in the formula to give a viscosity of 720 cps. This adhesive was designated T15765. The liner was coated with the adhesive at a thickness of 0.42 grams per 154.8 cm², on a 49" (1.24 m) wide web. The drying was done in heated air ovens with temperatures ranging from 82°C to 88°C. The adhesive was bonded to a 50μ cast vinyl. The critical test was to see how fast we could run while having a zero defects. Two liners were tried: the first being SCW1007 (Liner #1), the same used in Examples 1 to 5. A second liner (Liner #2) was tried because it is supplied from a different vendor, with a different silicone system. Both liners had the Comply™ and Controltac features. The results are shown in Table 2. One note is that for Example 6, 30 meters per minute ("mPm") was the highest speed reached before we ran out of material, there were no defects observed. On a subsequent experiment, 36.9 mPm was obtained with no defects.

Comparative Examples 6 and 7. For these examples, the Changeable Graphics Adhesive had no n-Octanol, but high amounts of ASE-60 to give a viscosity of 4000 cps. The adhesive is designated T15764. Results are in Table 2. For Comp. Ex. 6, the maximum 12.2 meters per minute ("mPm") has been verified over several factory experiments.

TABLE 2

Example #	Adh I.D.	Liner I.D.	n-Octanol	Viscosity (cps)	Max. Ctg. Speed (mPm)
Example 6	T15765	Liner #1	Yes 2.5%	720	30.0
Comp. Ex. 6	T15764	Liner #1	No	4000	12.2
Example 7	T15765	Liner #2	Yes 2.5%	720	21.3
Comp. Ex. 7	T15764	Liner #2	No	4000	9.14

As can be seen in Table 2, high viscosity alone does not guarantee good coating performance in a production situation. Also, the difference in silicone chemistry can have an effect on coating speed. However, the n-Octanol still provides a significant benefit.

Comparative Example 8 and Examples 8 to 46. These examples are summarized in Table 3. These samples are the same as Comp. Ex. 4 and Example 4, except for the additive changes as indicated.

TABLE 3

Example	Additive Name	Level (wt%)	Viscosity (cps)	Ctg. Wt. (gm)	Defects
Comp. Ex. 8	None	0	640	0.38	526
Example 8	n-Ethanol	2.5	380	0.36	41
Example 9	n-Propanol	2.5	420	0.37	0
Example 10	n-Butanol	1.0	430	0.37	0
Example 11	n-Butanol	2.5	450	0.36	0
Example 12	n-Hexanol	1.0	470	0.38	0
Example 13	n-Hexanol	2.5	540	0.38	0
Example 14	n-Octanol	1.0	510	0.38	0
Example 15	n-Octanol	2.5	590	0.38	0
Example 16	n-Decanol	2.5	650	0.40	0
Example 17	n-Dodecanol	2.5	>1000	0.40	>1000*
Example 18	iso-Propanol	2.5	380	0.38	178
Example 19	iso-Butanol	1.0	440	0.37	15
Example 20	iso-Butanol	2.5	330	0.38	1
Example 21	n-Hexyl Acetate	2.5	970	0.36	75
Example 22	n-Octanoic Acid	1.0	2500	0.38	0
Example 23	n-Octanoic Acid	2.5	>1000	0.38	0
Example 24	n-Heptane	2.5	>1000	0.38	1361
Example 25	n-Decane	2.5	>1000	0.36	313
Example 26	Toluene	2.5	>1000	0.40	175
Example 27	Methyl Ethyl Ketone	1.0	450	0.37	351
Example 28	Methyl Ethyl Ketone(1)	2.5	410	0.38	6
Example 29	TriEthanol Amine	2.5	480	0.37	408
Example 30	Ethylene Glycol	2.5	440	0.35	387
Example 31	Dowanol EB (2)	1.0	420	0.37	0
Example 32	Dowanol EB (2)	2.5	390	0.35	0
Example 33	Dowanol TPM (2)	2.5	360	0.34	0
Example 34	Dowanol DPM (2)	2.5	380	0.35	3
Example 35	Dowanol PMA (2)	2.5	370	0.36	2
Example 36	Surfynol 336PSA(3)	1.0	550	0.39	0
Example 37	Surfynol 336PSA(3)	2.5	840	0.39	0
Example 38	DowFax 2A1 (2, 4)	2.5	260	0.38	0
Example 39	Triton X151 (5)	2.5	280	0.38	44
Example 40	n-Hexyl Amine	2.5	Coagulated	NA	NA
Example 41	Cyclopentanol	2.5	570	0.36	57
Example 42	Cyclopentanol	5.0	570	0.35	4
Example 43	Phenethyl Alcohol	2.5	620	0.37	27
Example 44	Phenethyl Alcohol	5.0	710	0.35	0
Example 45	Cyclohexyl - 1-Propanol	2.5	700	0.38	128
Example 46	Cyclohexyl - 1-Propanol	5.0	830	0.37	0

Notes for Table 3

* - Many fine defects, but no large ones, appearance unacceptable

1 - Many fine coagulated particles in the adhesive.

2 - Dow Chemical Co., Midland, MI

5 3 - Air Products Co., Allentown, PA, Surfactant

4 - Anionic surfactant

5 - Rohm & Haas Co., Philadelphia, PA, Non-Ionic Surfactant

The rest of the materials can be purchased from any number of Chemical
10 Distributors, such as Aldrich Chemical Co., or J. T. Baker.

Comparative Example 9 and Examples 47-59. Same as Comp Ex 8 and Examples
8 to 46 except the experiment was done at a different time. The additives and
results are located in Table 4. Methanol and 1,4-Butanediol do not show any effect
15 in reducing defects. Ethanol, 3-Ethyl 1-Hexanol and Undecylenyl Alcohol (C11
with one unsaturation group) show a significant effect compared to the control in
reducing defects. N-Octanol also shows a significant effect even at 0.5 wt %.

TABLE 4

Example #		Wt%	Defects
C 9	None		922
47	Ethanol	5.0	71
48	n-Octanol	0.5	22
49	n-Octanol	5.0	0
50	n-Octanol	10.0	0
51	n-Octanol	15.0	0
52	n-Octanol	20.0	0
53	Methanol	2.5	>2000
54	Methanol	5.0	1010
55	3-Methyl 1-Butanol	2.5	0
56	3-Ethyl 1-Butanol	2.5	0
57	3-Ethyl 1-Hexanol	2.5	5
58	Undecylenyl Alcohol	2.5	24
59	1,4-Butanediol	2.5	1200

20

Comparative Example 10 and Examples 60-65. Same as Comp Ex 8 and
Examples 8 to 46 except Union Carbide R 9168(Union Carbide Corp., Cary, NC)
was substituted for Fastbond™ 49, and no extra water or ASE-60 thickener was
added. Results shown in Table 5. Both n-Butanol and n-Octanol showed good
25 effect, particularly at the 5 wt% level.

TABLE 5

Example #	Union Carbide R9168	Wt%	Defects	Tack (6 m)
C10	None	0.0	>5000	155
60	n-Butanol	2.5	92	
61	n-Butanol	5.0	0	145
62	n-Octanol	2.5	9	
63	n-Octanol	5.0	0	135
64	Dowanol EB	2.5	0	160
65	Dowanol EB	5.0	0	175

Comparative Example 11 and Examples 66-67. Same as Comp Ex 10 and

Examples 54 to 57 except, that Dynatech 1141 (Dyna-Tech Adhesives Inc., Grafton, WV), an SBR based adhesive, was used in place of R9168. The addition of n-Butanol caused the latex to coagulate, but the addition of n-Octanol did not cause any problems. As can be seen in the results in Table 6, the n-Octanol had a positive effect.

TABLE 6

Example #	Dynatech 1141 (SBR Latex)	Wt%	Defects
C 11	None	0.0	>1500
66	n-Butanol	2.5	Coag
67	n-Octanol	2.5	0

Comparative Example 12 and Examples 68-69. Same as Comp Ex 10 and

Examples 54 to 57 except, Airflex 420 (Air Products and Chemicals Inc., Allentown, PA) was used in place of R9168. Both n-Butanol and n-Octanol showed a positive effect. Results in Table 7.

TABLE 7

Example #	Airflex 420 (EVA)	Wt%	Defects
C12	None	0.0	200
68	n-Butanol	2.5	1
69	n-Octanol	2.5	0

Comparative Example 13 and Examples 70-71. Same as Comp Ex 8 and

Examples 8 to 46 except, that the adhesive was coated on a non-structured PolySlik™ (Rexam Release Corp., Iowa City, IA) liner at a nominal 0.38 grams

per 24 square inches. Results are shown in Table 8. The test for good coating was to see how far the adhesive would shrink in from the edge of the liner on a 30.5 cm coated web. The edge shrinkage value is an average of both sides. As can be seen in Table 8, 5 wt% n-Octanol reduced the edge shrinkage to 0.

5

TABLE 8

Example #	RD914	Wt%	Edge Shrinkage	
C 13	none		2.22	cm
70	n-Octanol	2.5	1.59	"
71	n-Octanol	5.0	0.00	"

Comparative Example 14 and Examples 72-73. Same as Comp Ex 13 and Examples 63 to 64 except, that R9168 was used as in Comp Ex 10. Results in Table 9. The n-Octanol did not completely eliminate the edge shrinkage, but reduced it significantly compared to the control. For Comp Ex 14, the result was that only the center 4 inches of the web had a continuous film of adhesive, with the outer 4 inches on either side being composed of individual droplets.

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TABLE 9

Example #	R9168	Wt%	Edge Shrinkage	
C14	none	0.0	10.16	cm
72	n-Octanol	2.5	2.54	"
73	n-Octanol	5.0	0.95	"

Comparative Examples 15 and 16 and Examples 74-88. Same as Comp Ex 8 and Examples 8 to 46 except, that an adhesive, called Changeable Graphics Adhesive ("CGA"), composed of Fastbond 49 and 3M hollow microspheres, was prepared with a number of additives as shown in Table 10. The CGA was prepared at a low viscosity in order to more easily discriminate between the effects of the additives in a lab experiment. Also in Table 10 are the number of defects per 24 sq. inches. Viscosity and coating weight data were omitted since they both varied in an acceptable range. In the additional columns in Table 10, the various adhesive performance properties are shown. Liner release is a measure of how easy it is to remove the product from the liner. The key performance property is that the liner release remain the same. The next column shows Probe Tack (ASTM D2979-71),

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which measures the initial "grab" of the adhesive. This test generally has a great deal of variability.

The last two columns show the 180 degree peel. The adhesive coated samples were applied to either Fruehauf painted aluminum (a common truck body material) or aluminum panels that had 3M 180-10 vinyl graphic film applied to the surface, the latter simulating overlaps when applying graphics. After application, the samples were subjected to 7 days water-soaking to simulate a severe weather condition. As can be seen in Table 10, the only additive that shows a severe negative effect is Surfynol 336, which illustrates the problems with surfactants.

TABLE 10

Example #	Additive	Wt%	Defects	Liner Release	Tack	FRUE-HAUF	180-10
				254 cm grams	Grams	7d/H ₂ O Avg (lbs/in)	7d/H ₂ O Avg (lbs/in)
C 15	None	0.0	>2000	15	130	1.4	3.0
74	n-Ethanol	1.0	130	15	120	1.3	2.4
75	n-Propanol	1.0	99	16	110	1.2	2.9
76	n-Butanol	1.0	118	15	125	1.2	2.5
77	n-Octanol	0.5	48	15	105	1.3	3.1
78	n-Octanol	1.0	0	16	130	1.5	3.0
79	n-Octanol	1.5	0	15	120	1.3	2.8
80	n-Octanol	2.5	0	16	125	1.3	2.7
81	iso-Propanol	1.0	6	15	110	1.4	3.0
82	iso-Butanol	1.0	16	15	110	1.3	2.2
83	Dowanol EB	1.0	0	16	100	1.4	2.4
84	Dowanol EB	2.5	0	15	120	1.2	2.2
85	Dowanol DPM	1.0	355	14	105	1.2	2.3
86	Dowanol PMA	1.0	200	15	120	1.4	2.6
87	Cellosolve Acetate	1.0	58	15	105	1.3	2.8
88	Cellosolve Acetate*	2.5	192	16	95	1.2	2.3
C16	Surfynol 336	1.0	0	18	110	0.1	0.7
	* - Starting to see coagulation with the addition of the additive						

Comparative Example 17 and Examples 89-97. Same as Comp Ex 15 and 16 and Examples 74 to 88 except, that prepared in a separate experiment, with the adhesive aging being only 4 days instead of 7. As can be seen in Table 11, Dowanol materials provide good reduction of defects compared to the control.

TABLE 11

Example #	Additive	Wt%	Defects	Tack (grams)	FRUE- HAUF 4d/H ₂ O Avg (lbs/in)	180-10 4d/H ₂ O Avg (lbs/in)
C17	None	0	>2000	130	1.0	2.9
89	n-Octanol	5.0	0	110	0.6	2.9
90	Dowanol EB	2.5	0	110	0.7	3.1
91	Dowanol EB	5.0	0	115	0.6	3.0
92	Dowanol EB	10.0	0	115	0.7	2.9
93	Dowanol DB	2.5	0	115	0.8	3.1
94	Dowanol DM	2.5	65	115	0.9	3.1
95	Dowanol DPnB	2.5	0	95	0.5	2.9
96	Dowanol PPH	2.5	3	120	0.8	3.2
97	Dowanol TPnB	2.5	0	100	0.6	2.8

5 Detailed Description of Drawing

Fig. 1 is a side-by-side photograph of two adhesives coated on non-flat liners. Adhesive/liner composite 10 corresponds to comparative Example 1. Defects 15 are apparent, which are locations on the structured liner where no adhesive is present. Adhesive/liner composite 20 corresponds to Example 1. No defects are visible in this composite 20.

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Claims:

1. A coatable adhesive comprising
a latex adhesive and a coating-enhancing amount of a linear or
5 branched, optionally unsaturated, alkyl mono-alcohol, said alcohol being a liquid at
25°C.
2. The adhesive of claim 1, wherein the alcohol is selected from C3-C10
linear or branched mono-alcohols.
- 10 3. The adhesive of claim 1, wherein the alcohol is selected from C6-C10
linear or branched mono-alcohols
4. The adhesive of claim 1, wherein the alcohol is present as 0.5-20 % by
15 weight.
5. The adhesive of claim 1, wherein the alcohol is present as 1-5 % by
weight.
- 20 6. The adhesive of claim 1, wherein the latex adhesive comprises a
polymer selected from the group consisting of styrene-butadiene rubber, acrylic,
neoprene and vinyl acetate-ethylene.
- 25 7. The adhesive of claim 1, wherein the latex adhesive comprises a
polymer selected from the group consisting of butadiene and acrylonitrile
copolymers, butadiene with styrene and acrylonitrile, chloroprene copolymers,
methacrylate and acrylate ester copolymers, vinyl acetate copolymers, vinyl and
vinylidene chloride copolymers, ethylene copolymers, fluorinated copolymers,
acrylamide copolymers, styrene-acrolein copolymers, pyrrole and pyrrole
30 copolymers, and poly(vinyl acetate)-poly(vinyl alcohol) copolymers.

9. The adhesive of claim 1, wherein the latex adhesive is a pressure-sensitive adhesive after being applied to a backing.

5 10. The adhesive of claim 1, wherein the latex adhesive is a heat-activated adhesive after being applied to a backing.

 11. A method of improving coatability of a latex adhesive, comprising adding a coating-enhancing amount of a linear or branched optionally unsaturated
10 mono-alcohol to said latex adhesive, said alcohol being a liquid at 25°C.

 12. The method of claim 11, wherein the alcohol is selected from C3-C10 linear or branched mono-alcohols.

15 13. The method of claim 11, wherein the alcohol is selected from C6-C10 linear or branched mono-alcohols.

 14. The method of claim 11, wherein the alcohol is present as 0.5-20 % by weight.

20 15. The method of claim 11, wherein the alcohol is present as 1-5 % by weight.

 16. The method of claim 11, wherein the latex adhesive comprises a
25 polymer selected from the group consisting of styrene-butadiene rubber, acrylic, neoprene and vinyl acetate-ethylene.

 17. The method of claim 11, wherein the latex adhesive comprises a
30 polymer selected from the group consisting of butadiene and acrylonitrile copolymers, butadiene with styrene and acrylonitrile, chloroprene copolymers, methacrylate and acrylate ester copolymers, vinyl acetate copolymers, vinyl and vinylidene chloride copolymers, ethylene copolymers, fluorinated copolymers,

acrylamide copolymers, styrene-acrolein copolymers, pyrrole and pyrrole copolymers, and poly(vinyl acetate)-poly(vinyl alcohol) copolymers.

18. An adhesive composite, comprising

- 5 a) a low energy sheet material having a first major surface and a second major surface,
- b) a latex adhesive coated on the first major surface of the low energy sheet material from an adhesive composition of claim 1,
- c) a backing layer having a first major surface and a second major
- 10 surface, the second major surface being in contact with said coated latex adhesive.

19. The adhesive composite of claim 18, wherein the first major surface of the low energy sheet material is selected from the group consisting of polyolefin plastics, glass, and liners made of kraft papers, polyethylene, polypropylene,

15 polyester or composites of any of these materials, wherein the liners are coated with a release agent selected from fluorochemicals and silicone.

20. The adhesive composite of claim 18, wherein the latex adhesive comprises a polymer selected from the group consisting of styrene-butadiene rubber, acrylic, neoprene and vinyl acetate-ethylene.

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21. The adhesive composite of claim 18, wherein the latex adhesive comprises a polymer selected from the group consisting of butadiene and acrylonitrile copolymers, butadiene with styrene and acrylonitrile, chloroprene

25 copolymers, methacrylate and acrylate ester copolymers, vinyl acetate copolymers, vinyl and vinylidene chloride copolymers, ethylene copolymers, fluorinated copolymers, acrylamide copolymers, styrene-acrolein copolymers, pyrrole and pyrrole copolymers, and poly(vinyl acetate)-poly(vinyl alcohol) copolymers.

22. The adhesive composite of claim 18, wherein the backing layer is selected from the group consisting of polyesters, polyolefins, papers, cardboard,

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foils, polyacrylates, polyurethanes, perfluoropolymers, polycarbonates, ethylene vinyl acetates, and combinations thereof.

23. The adhesive composite of claim 18, wherein the backing layer is
5 selected from the group consisting of vinyl films, woven and nonwoven sheets, woven and nonwoven fabrics, papers and retroreflective sheeting.

24. The adhesive composite of claim 18, wherein the low energy sheet
material is a structured liner.

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25. An adhesive/liner construction, comprising an adhesive that has been coated on a structured liner, said adhesive comprising

a latex adhesive and a coating-enhancing amount of a linear or
branched, optionally unsaturated, mono-alcohol, said alcohol being a liquid at
15 25°C, and said alcohol optionally being interrupted with one or more oxygens, said alcohol being present in an amount such that said adhesive exhibits fewer defects as compared to the same adhesive formulation that does not contain the coating-enhancing alcohol in a Standard Defect Evaluation, and said adhesive has a 180°
20 peel value that is no less than 80% of the same adhesive formulation that does not contain the coating enhancing alcohol additive.

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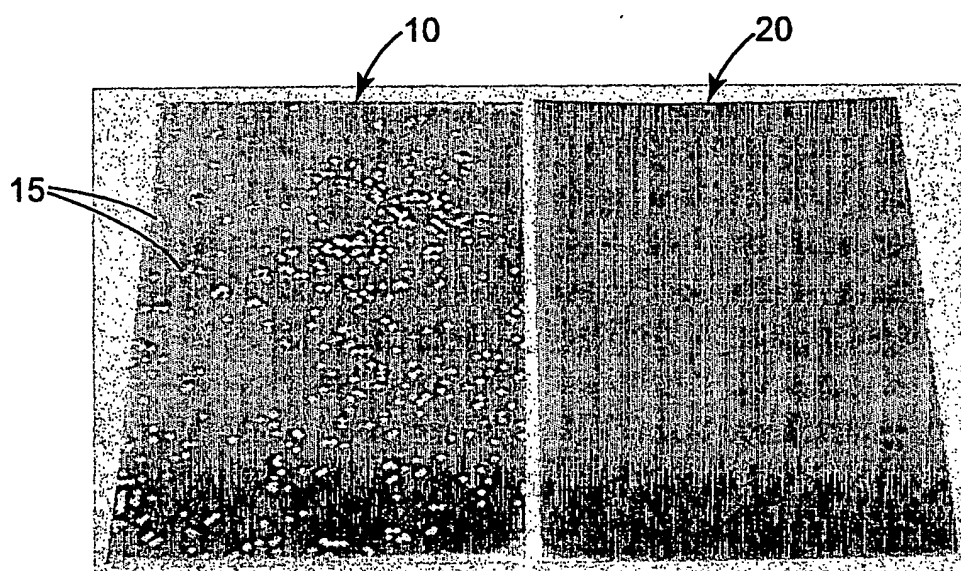


Fig. 1

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 00/24444

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09J7/02 C09J201/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 380 938 A (JACK JAMES ET AL) 30 April 1968 (1968-04-30) claim 2; examples 1,2 -----	1-5,7,9

☐ Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
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- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
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- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

2 January 2001

Date of mailing of the international search report

17. 01. 2001

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Schueler, D

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 00/24444

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/SA/ 210

Continuation of Box I.2

Present claims 1 and 25 relate to a product/compound defined by reference to a desirable characteristic or property, namely "an coating enhancing amount of alcohol".

The claims cover all products/compounds having this characteristic or property, whereas the application provides support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT for only a very limited number of such products/compounds. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Independent of the above reasoning, the claims also lack clarity (Article 6 PCT). An attempt is made to define the product/compound by reference to a result to be achieved. Again, this lack of clarity in the present case is such as to render a meaningful search over the whole of the claimed scope impossible. Consequently, the search has been carried out for those parts of the claims which appear to be clear, supported and disclosed, namely those parts relating to the products/compounds mentioned in the description in table 3, ex. 8-20; table 4, ex. 55-58; at a concentration falling within the limits given in claim 4.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/24444

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3380938 A	30-04-1968	NONE	

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